PB-216 644

# ATMOSPHERIC EMISSIONS FROM CATALYTIC CRACKING UNIT REGENERATOR STACKS

Victor H. Sussman

Joint District, Federal and State Project for the Evaluation of Refinery Emissions

June 1957

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

PB 216 644

JOINT DISTRICT, FEDERAL AND STATE PROJECT
FOR THE EVALUATION OF REFINERY EMISSIONS

REPORT NUMBER 4
June, 1957

# ATMOSPHERIC EMISSIONS FROM CATALYTIC CRACKING UNIT REGENERATOR STACKS

by

Victor H. Sussman

Details of illustrations in this document may be better studied on microfiche

PARTICIPATING AGENCIES

AIR POLLUTION CONTROL DISTRICT, COUNTY OF LOS ANGELES
LESLIE A. CHAMBERS, Director, Research Division
CARL V. HANTER, Chairman, Joint Project Committee

STATE OF CALIFORNIA, DEPARTMENT OF PUBLIC HEALTH
JOHN A. NAGA, Chief, Bureau of Air Sanitation

U.S. DEPARTMENT OF HEALTH, EDUCATION AND WELFARE, PUBLIC HEALTH SERVICE
ANDREW H. ROSE, JR., Chief, Engineering Research and Development Section, Community Air Pollution Program

WESTERN OIL AND GAS ASSOCIATION, AIR POLLUTION CONTROL COMMITTEE
GERALD FISHER, Chairman, Technical Subcommittee

Reproduced by
NATIONAL TECHNICAL INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

# FOREWORD

In August 1955, the Los Angeles County Air Pollution Control District, the California State Department of Public Health, and the U. S. Public Health Service inaugurated the Joint District, Federal, and State Project for the Evaluation of Refinery Emissions in Los Angeles County. The Western Oil and Gas Association, representing the petroleum industry, also participated in the project. This report presents the results of one of the studies of the Joint Project.

# ATMOSPHERIC EMISSIONS FROM CATALYTIC CRACKING UNIT REGENERATOR STACKS

IN BRIEF:

The refineries in Los Angeles County operate six Fluid Catalytic Cracking Units, nine Thermofor Catalytic Cracking Units, and one Thermofor Catalytic Reforming Unit. These units process approximately 241,000 BPD of petroleum distillate.

The atmospheric effluents from the regenerator stacks of these units were tested. Individual and total emission rates from these stacks are presented along with details of the sampling techniques and analytical methods used to obtain these data.

The total emission rates from the regenerator stacks of the Thermofor and Fluid Catalytic Cracking Units (excluding the TCR Unit) were found to be of the order of -

| | |
|---|---|
| Particulate Matter | 5 tons/day |
| Sulfur Trioxide | 3 tons/day |
| Sulfur Dioxide | 43 tons/day |
| Ammonia | 4 tons/day |
| Cyanides (as HCN) | 24 lb./day |
| Aldehydes (as HCHO) | 2 tons/day |
| Oxides of Nitrogen (as $NO_2$) | 5 tons/day |
| Hydrocarbons | 20 tons/day |

TABLE OF CONTENTS


| | Page |
|---|---|
| Introduction | 1 |
| Sampling and Analytical Methods | 3 |
| Determination of Stack Gas Velocity | 3 |
| Sampling Equipment | 5 |
| Outline of Sampling Method | 5 |
| Field Sampling Data and Calculations | 9 |
| Outline of Analytical Methods | 12 |
| Results and Discussion | 15 |
| Description of Units Tested and Test Assemblies | 15 |
| Studies of Sampling Methods | 18 |
| Efficiency of Collection of Oxides of Sulfur | 18 |
| Efficiency of Distilled Water in the Collection of Compounds of Ammonia | 18 |
| Particulate Matter | 19 |
| Percent Loss on Ignition | 21 |
| Location of Alundum Thimble | 23 |
| Hydrocarbons | 23 |
| Sulfur Oxides, Ammonia, Cyanides, Aldehydes, Oxides of Nitrogen, $CO_2$, $O_2$, and CO | 26 |
| Organic Acids | 30 |
| Catalyst Elevator Vents | 30 |
| Totals and Summation | 32 |
| Appendix (Analytical Procedures)-- Table of Contents | 34 |
| Acknowledgement | 54 |

## LIST OF TABLES AND FIGURES

TABLES:


| | | Page |
|---|---|---|
| Table I - | Velocity Traverse Points | 3 |
| Table II - | Velocity Traverse Data | 4 |
| Table III - | Meter Rate Pressure Correction | 11 |
| Table IV - | Typical Field Test Data Sheet | 13 |
| Table V - | Operating Characteristics of Units Tested | 16 |
| Table VI - | Insoluble Solids and Residue on Evaporation to Dryness in $H_2O$ and HCl Impinger Solutions | 20 |
| Table VII - | Particulate Matter | 21 |
| Table VIII - | Percent Loss of Particulate Matter on Ignition | 22 |
| Table IX - | Hydrocarbon Emissions | 24 |
| Table X - | Sulfur Oxides, Ammonia, and Cyanides | 27 |
| Table XI - | Aldehydes, Oxides of Nitrogen, $CO_2$, $O_2$, CO, and $N_2$ | 28 |
| Table XII - | Per cent Moisture and Flue Gas Volumes | 29 |
| Table XIII - | TCC Elevator Vents | 31 |
| Table XIV - | Total Emission Rates | 33 |

FIGURES:


| | | Page |
|---|---|---|
| Figure 1- | Catalytic Cracking Units | 1 |
| Figure 2 - | Sampling Train | 7 |
| Figure 3 - | Alundum Thimble and Disassembled Holder | 8 |
| Figure 4 - | Alundum Thimble Sampling Train | 8 |
| Figure 5 - | Bottle Used to Collect Stack Gases for Orsat Determination | 10 |
| Figure 6 - | Grab Sampling Bulbs | 10 |

# ATMOSPHERIC EMISSIONS FROM CATALYTIC CRACKING UNIT REGENERATOR STACKS

## INTRODUCTION

During the process of the catalytic cracking of petroleum distillates to obtain high octane gasoline, coke is formed on the surface of the catalyst. The coke is burned off in a regenerator vessel by passing air through the hot catalyst. Steam is sometimes injected into the vessel to control the temperature of the hot catalyst. The flue gases thus generated contain not only the products of combustion of the coke (which contains many of the impurities found in the stock being cracked) but also some fine catalyst dust.

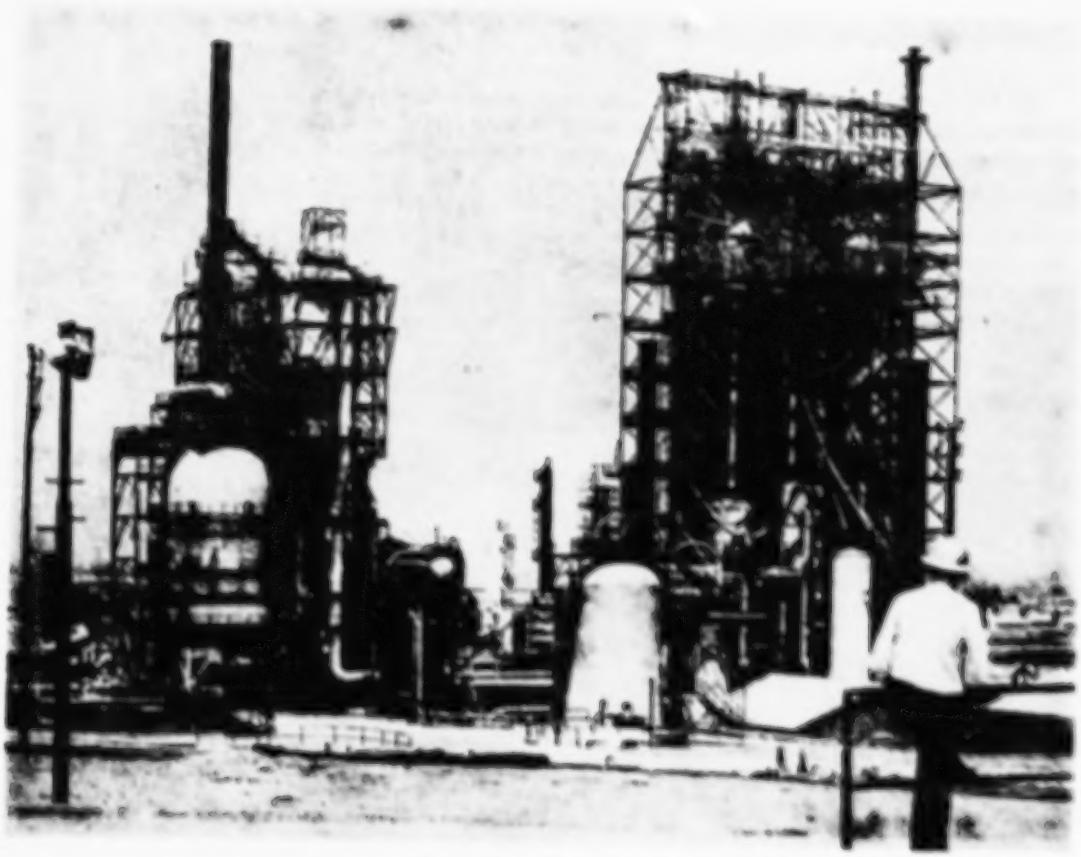

**Figure 1.**

**Catalytic Cracking Units. Fluid Catalytic Cracking Unit on left; Twin Thermofor Catalytic Cracking Units on right.**



Reproduced from best available copy.

It is the practice of refineries in Los Angeles County to pass the regenerator flue gases through an external air cleaning device before discharging to the atmosphere. When electrostatic precipitators are used as collectors, it is sometimes necessary to inject ammonia into the gas stream to increase collection efficiency.

In order to determine the quantity and nature of the substances released to the atmosphere from catalytic cracking unit regenerator stacks, a testing program was initiated by the Joint District, Federal and State Project for the Evaluation of Refinery Emissions.

There are six fluid catalytic cracking units (FCC), nine Thermofor catalytic cracking units (TCC), and one Thermofor catalytic reforming unit (TCR) operating within Los Angeles County. All units were tested, beginning with the first test on August 30, 1956, and ending with the last test on December 19, 1956.

The following determinations were made on the flue gases from each regenerator stack:

Aldehydes (as HCHO)
Ammonia
Carbon monoxide, carbon dioxide, oxygen, and nitrogen (by Orsat)
Cyanides (as HCN)
Hydrocarbons, by Infrared Spectrophotometer and Mass Spectrometer Analysis
Organic acids (as $CH_3COOH$)
Oxides of nitrogen (as $NO_2$)
Oxides of sulfur, $SO_3$ and $SO_2$
Total particulate matter and percent lost on ignition
Total volume of stack gas and percent moisture

## SAMPLING AND ANALYTICAL METHODS

### Determination of Stack Gas Velocity:*

In order to determine the total amount and concentration of stack emissions it is necessary to first determine the stack gas flow rates. It is also necessary, if isokinetic sampling is to be performed, to know the velocity at the sampling point.

A convenient stack sampling point is chosen in a region of uniform flow. The velocity of the effluent stream is measured by making a number of Pitot tube traverses (three along the diameter through the sampling hole and three at right angles to this traverse line). As an example, a typical set of actual field test data are presented below:

Inside diameter of the stack = 41.1 inches.

An "S" type Pitot tube was used having a factor of 0.835, i.e., 0.835 x velocity (apparent) = actual velocity.

The cross-sectional area of the stack was divided into four equal annular concentric areas and the distances from the inside circumference to the traverse points (the centers of these areas) are as follows:

TABLE I

Velocity Traverse Points

| Points | % I.D. | Distance, Inches |
|---|---|---|
| 1, 9 | 3.3 | 1.35 |
| 2, 10 | 10.5 | 4.3 |
| 3, 11 | 19.5 | 8.0 |
| 4, 12 | 32.1 | 13.3 |
| 5, 13 | 67.9 | 28.2 |
| 6, 14 | 80.5 | 33.0 |
| 7, 15 | 89.5 | 36.7 |
| 8, 16 | 96.7 | 39.7 |

A thermocouple was inserted into the stack and placed near point 1. The data were recorded as shown in Table II.

---

* For a more detailed description of stack sampling methods and techniques see Kanter, et al., "Techniques of Testing for Air Contaminants from Combustion Sources", Journal of the A.P.C.A., Vol. 6, No. 4, Feb. 1957, pp. 191-199.

## TABLE II

### Velocity Traverse Data

**(as taken during an actual test)**

| | Run 1 | | Run 2 | | Run 3 | | |
|---|---|---|---|---|---|---|---|
| Point | Velocity Head In. $H_2O$ | Temp. Stack $^oF$ | Velocity Head In. $H_2O$ | Temp. Stack $^oF$ | Velocity Head In. $H_2O$ | Temp. Stack $^oF$ | Velocity Ft./Sec. @ 680$^oF$ |
| 1 | 0.62 | 670 | 0.58 | 670 | 0.60 | 680 | 63 |
| 2 | 0.80 | 670 | 0.82 | 670 | 0.82 | 680 | 73 |
| 3 | 0.89 | 670 | 0.90 | 670 | 0.91 | 680 | 77 |
| 4 | 0.91 | 670 | 0.91 | 670 | 0.91 | 680 | 78 |
| 5 | 0.90 | 670 | 0.95 | 670 | 0.92 | 680 | 78 |
| 6 | 0.89 | 670 | 0.88 | 670 | 0.89 | 680 | 77 |
| 7 | 0.81 | 670 | 0.79 | 670 | 0.80 | 680 | 73 |
| 8 | 0.55 | 670 | 0.65 | 670 | 0.62 | 680 | 64 |
| 9 | 0.55 | 680 | 0.57 | 690 | 0.63 | 690 | 62 |
| 10 | 0.79 | 680 | 0.76 | 690 | 0.79 | 690 | 72 |
| 11 | 0.88 | 680 | 0.89 | 690 | 0.86 | 690 | 76 |
| 12 | 0.90 | 680 | 0.94 | 690 | 0.91 | 690 | 78 |
| 13 | 0.93 | 680 | 0.94 | 690 | 0.90 | 690 | 78 |
| 14 | 0.91 | 680 | 0.88 | 690 | 0.86 | 690 | 76 |
| 15 | 0.78 | 680 | 0.80 | 690 | 0.83 | 690 | 73 |
| 16 | 0.61 | 680 | 0.58 | 690 | 0.63 | 690 | 64 |

The velocity head is read in inches of water from an inclined manometer. The velocity in feet per second (shown in the extreme right column) is obtained from the average of the three velocity head values for each point at an average temperature. The Pitot correction factor is incorporated as described previously. Using the average of the velocity heads at an average temperature to obtain the velocity at a point is not precise. Each velocity head value should first be converted into its corresponding velocity and the average of these velocities used. However, in this series of tests, where the velocity head and temperature did not vary excessively with time, this expedient was found to be accurate within the limits of the test.

The average of the velocities shown in the extreme right column of Table II is 72.6. A point of average velocity is used for sampling and point number 10 was chosen, since the velocity at that point (72 feet per second) is close to the average, and at a convenient distance from the sampling hole.

Calculations and test methods employed in the isokinetic sampling of this stack are discussed in the section headed "Field Sampling Data and Calculations".

Sampling Equipment:

The following items of equipment are required for each stack test:

Glass sampling probe
Stainless steel sampling probe
Whatman thimble, single thickness 43 mm x 123 mm
Whatman thimble, double weight 43 mm x 123 mm
Alundum thimble--porosity RA 98 coarse, 45 mm OD x 127 mm ht.
Vacuum pump, or air aspirator
Six 500-ml impingers
Integrating type dry gas meter
Mercury manometer
Thermometer
Evacuated bulbs--300-ml mine sampling tubes and two-liter round bottom flasks
Pitot tube and inclined manometer
Whatman and Alundum thimble holders
Ice bath container
Thermocouple pyrometer

Outline of Sampling Method:

Sampling for particulate matter, ammonia, oxides of sulfur, organic acids and cyanides is carried on simultaneously and continuously for a period of one hour with two parallel sampling trains. A gas sample for Orsat analysis is collected by a liquid displacement method. During the sampling period, grab samples for aldehydes, oxides of nitrogen and hydrocarbons are taken.

The sampling trains are assembled as shown in Figure 2.

The probes are placed within the stack and the thimble holders remain outside of the stack. The thimble holders are insulated with asbestos cloth. A heating unit may also be used to keep the temperature within the holder above the dew point* of the stack gases. A heating unit was not used during this series of tests. The two trains following the sampling probes (1)** are:

A. Train used for particulate matter and ammonia

An Alundum thimble (2) with a pyrex glass wool lining (see Figure 3) followed by three 500-ml. impingers (3) immersed in an ice bath (4). The first impinger contains 100 ml. of distilled water. The second impinger contains 100 ml. of a 5% solution of HCl. The last impinger is dry and is provided with a thermometer (5). The impinger section is followed by a manometer (6), meter (7), and vacuum pump (8). A hose clamp (9) is used to control the gas flow rate. Figure 4 shows an assembled Alundum thimble train.

Particulate matter is determined from the Alundum thimble catch and material filtered from the $H_2O$ and HCl impinger solutions. $NH_3$ is determined from the $H_2O$ and HCl impinger solutions.

B. Train used for sulfur oxides, organic acids and cyanides

A double thickness Whatman paper thimble (2) followed by three 500-ml. impingers (3) immersed in an ice bath (4). The first two impingers each contain 100 ml. of a 5% solution of NaOH. The third impinger is dry and is provided with a thermometer (5). Following the impinger section is a single thickness Whatman paper thimble (2a), a manometer (6), a meter (7), and a vacuum pump (8).

---

* In this discussion the term "Dew Point" refers to the temperature of condensation of water vapor only.

** Numbers in parentheses refer to Figure 2, page 7

$SO_3$ is determined from the Whatman thimble catch. $SO_2$, Organic Acids, and Cyanides are determined from the NaOH impinger solutions. The purpose of the single weight Whatman thimble following the NaOH impinger assembly is to test the efficiency of the impinger solution and double weight Whatman thimble for the collection of $SO_3$.

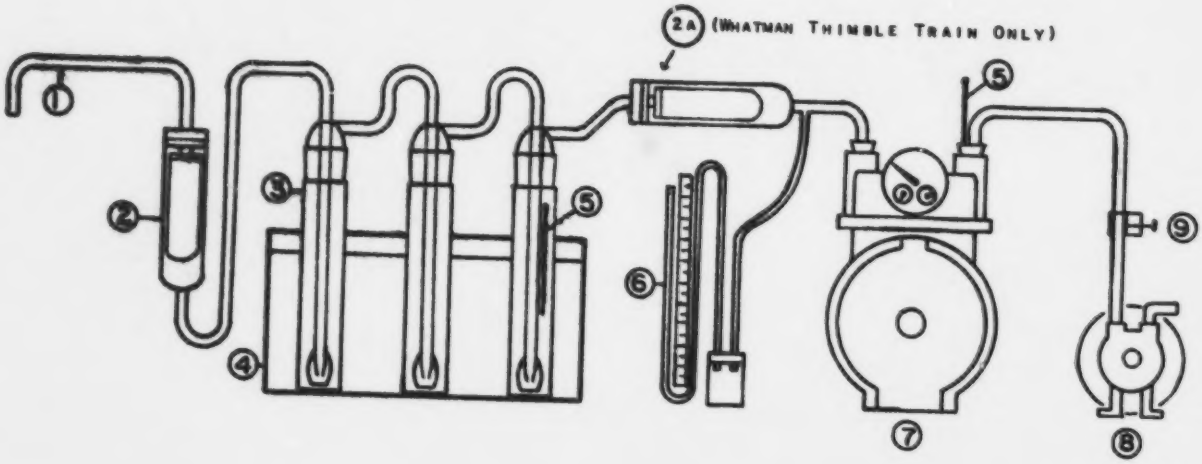


Figure 2.

Sampling Train

Both the Alundum thimble train and the Whatman thimble train are represented in Figure 2. A single weight Whatman thimble (2A) is inserted after the last impinger in the Whatman train only.

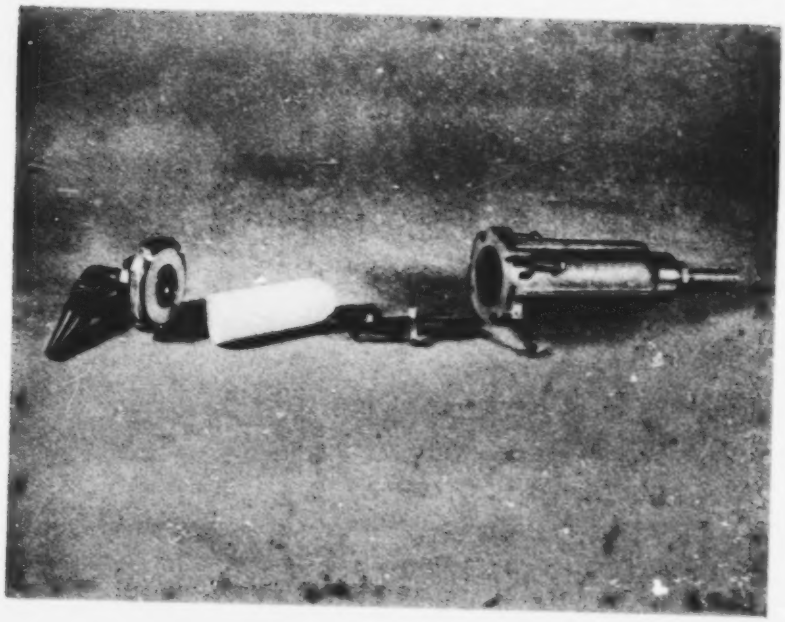

Figure 3.

Alundum Thimble and Disassembled Holder. Sampling nozzle is shown inserted in holder cap. During the test the nozzle was placed at the end of the probe.

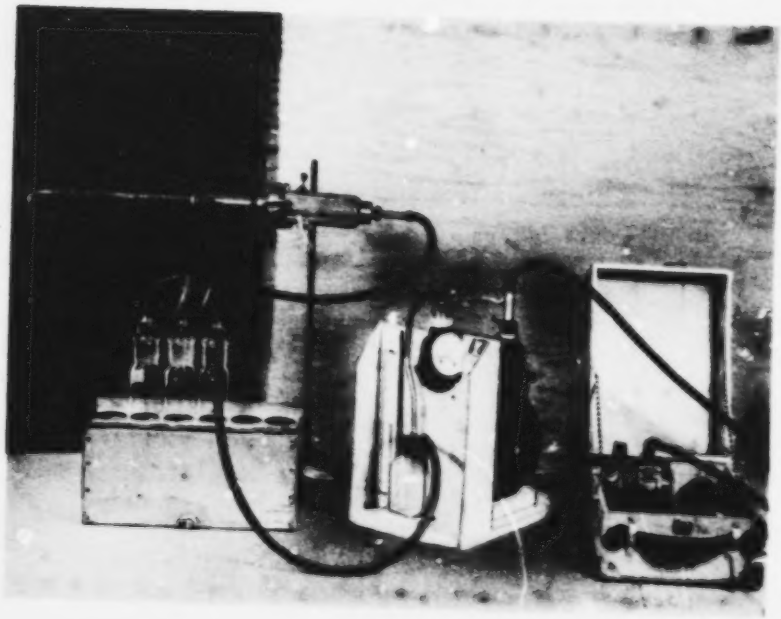

Figure 4.

Alundum Thimble Sampling Train provided with Vycor Glass Sampling Probe.

## Collection of Gas Sample for Orsat Determination:

An integrated gas sample for Orsat analysis (carbon monoxide, carbon dioxide, oxygen and nitrogen) is collected by withdrawing gases continuously from the stack at a constant rate by liquid displacement. A five-liter bottle filled with a saturated sodium sulfate solution, slightly acidified with sulfuric acid, is used as the gas holder (see Figure 5). As the solution siphons out, the gas sample is drawn into the bottle. The rate of siphoning is adjusted so that a gas sample of about four liters is obtained during the course of the test. The sample is drawn from the same stack cross section used for collecting the particulate matter.

## Collection of Gas Samples for Aldehydes; Oxides of Nitrogen and Hydrocarbons:

During the sampling period, four grab samples (see Figure 6) are taken at the end of every 15-minute interval as follows:

Aldehydes: A gas sample is drawn into a two-liter evacuated flask containing 10 ml. of a 1% solution of sodium bisulfite.

Oxides of Nitrogen: A gas sample is drawn into a two-liter evacuated flask containing 25 ml. of a solution of hydrogen peroxide and sulfuric acid. The absorbing solution is prepared by adding 1 ml. of 3% $H_2O_2$ to 100 ml. of 0.1N $H_2SO_4$.

Hydrocarbons: Two gas samples are taken. One sample is collected in a dry evacuated two-liter flask. This sample is analyzed in an Infrared Spectrophotometer and reported as hexane. The second sample is collected in a 300-ml. dry evacuated Mine Sampling Tube. This sample is analyzed by Mass Spectrometer.

## Field Sampling Data and Calculations:

A typical field data sheet and set of calculations for determining the isokinetic sampling rate are presented below.

The method used and data recorded for the determination of the velocity and the sampling point in a stack has been presented. It is now necessary to determine the diameter of the sampling nozzle and the sampling rate (as recorded at the meter) in order to obtain isokinetic conditions.

Point 10 having a velocity of 72.0 feet per second was chosen in the 41.1 inch I.D. stack.

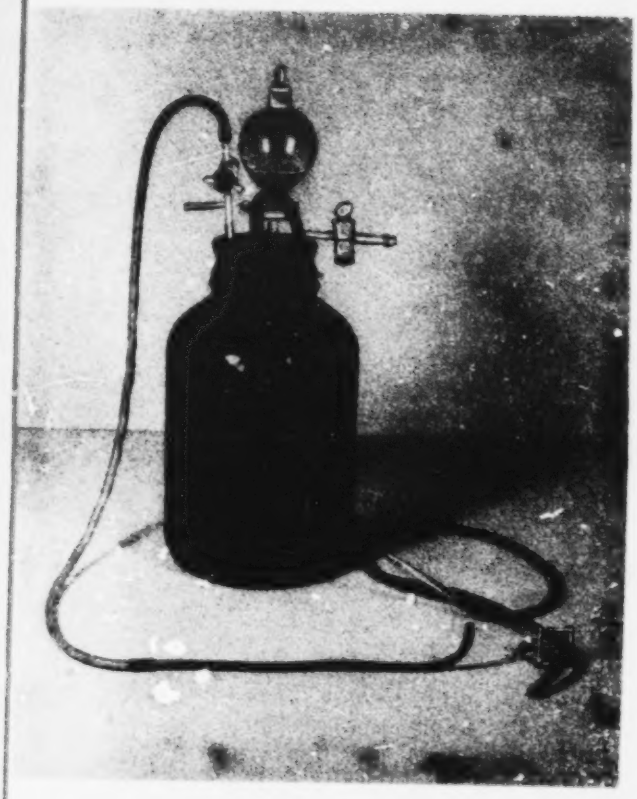

Figure 5. Bottle used to collect stack gases for subsequent Orsat determination ←

Figure 6. Grab Sampling Bulbs. Two liter round bottom flask above, 300-ml. Mine Sampling Tube (used in obtaining sample for Mass Spectrometer analysis) below. →

The equation used to predetermine the optimum meter sampling rate is--

$$M = \frac{\pi d^2}{4 \times 144} \times V \times 60 \times \frac{T_m}{T_s} = 0.33 \frac{T_m}{T_s} Vd^2$$

where:

M = meter rate, cubic feet per minute
$T_m$ = temperature in meter, degrees R.
$T_s$ = temperature in stack, degrees R.
V = velocity of stack gases, feet per second
d = diameter of sampling nozzle, inches

There are three unknown quantities in this equation: M, $T_m$, and d. $T_m$ is assumed to be 85°F. for purposes of calculation. The nozzle diameter is chosen to give a sampling rate, at isokinetic conditions, of between 0.7 and 1 CFM (the best rate for efficient collection in the thimble and trains).

Therefore; if a nozzle diameter of 1/4 inch is selected:

$$M = 0.33 \frac{545}{1140} \times 72.0 \times (1/4)^2 = 0.71 \text{ CFM}$$

It is necessary to correct for moisture condensing between the probe and the meter. Past tests showed the moisture content in the stack used as an example, to be approximately 7% by volume. Therefore, the corrected meter rate = 0.72 x 0.93 = 0.66.

The pressure varies at the meter as particulate matter is built up in the thimble and in order to maintain a sampling nozzle velocity of 72.0 feet per second, the following predetermined chart is used for this particular test:

TABLE III

Meter Rate Pressure Correction

| Vacuum at the Meter Inches Hg | Meter Rate CFM |
|---|---|
| 0 | 0.66 |
| 1 | 0.67 |
| 2 | 0.70 |
| 3 | 0.72 |
| 4 | 0.75 |
| 5 | 0.78 |
| 6 | 0.81 |
| 7 | 0.85 |
| 8 | 0.89 |
| 9 | 0.93 |

Thus when the manometer at the meter shows a vacuum of three inches Hg, the meter rate must be adjusted to 0.72 CFM. The test data are recorded as shown in Table IV, page 13.

Outline of Analytical Methods:

Many of the analytical methods used are standard and commonly employed in routine laboratory analysis. The following is an outline of the analytical methods used during this testing program. Detailed descriptions of the analytical procedures are listed in the Appendix of this report.

Alundum Thimble: The particulate matter in the thimble is weighed and then ignited at 1000°F. Weight of particulate matter collected and loss of weight on ignition are reported. Before and after sampling, the Alundum thimble is heated for one-half hour at 105°C and cooled in a desiccator before weighing.

Impinger train (water-HCl): The increase in volume of the impinger solutions is measured and, with the temperature and pressure of the saturated gas in the dry impinger is used to determine the per cent moisture in the stack gas. The impinger solutions are filtered separately and the residues weighed. An aliquot of the combined, filtered impinger solutions is made alkaline with sodium hydroxide and distilled into a standard $H_2SO_4$ solution, which is then back titrated using a standard sodium hydroxide solution, for the determination of ammonia.

Double weight Whatman paper thimble: The $SO_3$ (present as $H_2SO_4$) is extracted with water in a Soxhlet extraction unit and determined gravimetrically.

Impinger train (5%NaOH): The impinger solution is used for three determinations:

Total Dissolved Oxides of Sulfur. An aliquot is oxidized and the sulfur oxides are determined gravimetrically.

Organic Acids: (See page 30)

Cyanides. An aliquot is treated with acid, steam distilled into a sodium carbonate solution and the solution reacted with picric acid. The concentration is determined colorimetrically.

TABLE IV

Typical Field Test Data Sheet

Meter No. 19
Train Particulate, $NH_3$, Alundum
Point 10
Nozzle I.D. 1/4"
Orsat Collector No. 10
Thimble No. 1

| Time | Meter Reading Ft3 | Meter Vacuum In. Hgm | $T_{meter}$ $^oF$ | $T_{impinger}$ $^oF$ | $T_{stack}$ $^oF$ |
|---|---|---|---|---|---|
| 0 | 66.54 | | | | |
| + 5 | 69.5 | 4.0 | 92 | 58 | 710 |
| +10 | 73.7 | 6.0 | 92 | 58 | 710 |
| +15 | 76.7 | 6.0 | 94 | 56 | 710 |
| +20 | 81.5 | 5.0 | 95 | 57 | 710 |
| +25 | 84.0 | 5.0 | 96 | 57 | 710 |
| +30 | 88.5 | 6.5 | 94 | 57 | 710 |
| +35 | 92.2 | 6.5 | 92 | 57 | 710 |
| +40 | 96.3 | 6.5 | 90 | 58 | 710 |
| +45 | 100.5 | 6.5 | 90 | 56 | 710 |
| +50 | 104.6 | 6.5 | 90 | 56 | 710 |
| +55 | 108.7 | 6.5 | 90 | 56 | 710 |
| +60 | 112.82 | 6.5 | 91 | 56 | 710 |

Grab Samples:

Aldehydes. The sodium bisulfite-aldehyde complex is determined by an iodine titration.

Oxides of Nitrogen. The absorbing solution is made alkaline and evaporated to dryness. Phenoldisulfonic acid solution is added to the residue and the determination of the total oxides of nitrogen is made by measuring the light absorption of the resulting yellow solution, in a photoelectric colorimeter.

Hydrocarbons. The gas sample collected in the two-liter dry evacuated flask is purged into an Infrared Spectrophotometer and analyzed for total hydrocarbons as hexane.

The gas sample collected in the 300-ml. dry evacuated Mine Sampling Tube is analyzed in a Mass Spectrometer for the $C_1$, $C_2$, $C_3$, $C_4$, $C_5$, $C_6$ aliphatic hydrocarbons, benzene, and toluene.

## RESULTS AND DISCUSSION

### Description of Units Tested and Test Assemblies:

Code numbers have been assigned to the various catalytic cracking units. These numbers will be used to identify the units when presenting the results of the testing program. The letters F, T or R at the end of each coding designates FCC, TCC or TCR respectively.

Table V presents the operating characteristics of these units. The units are listed in order of the dates they were tested. All the data in Table V, except for the flue gas temperature which was measured by the test team, were supplied by the various companies whose units were tested.

The physical arrangement of the unit being tested made it impossible at times to sample at the most desirable point. There were instances when only one of two stacks of a regenerator unit was sampled, when the sampling point was not in the region of least turbulence, or when the probe of each train was located at a different sampling point.

The following list of sampling conditions is important to an understanding of the data presented and should be referred to when examining the results. Only the units having unusual setups or testing procedures are discussed. All TCC units are equipped with cyclone collectors and all FCC units are equipped with electrostatic precipitators.

Unit C-F: This unit is equipped with two stacks. A complete sampling program was carried out at one stack, while only velocity measurements, Orsat and grab samples were taken at the other stack. The results shown for total emissions (of substances sampled for by both trains) from this unit are based on the measurements made on one stack. These results were extrapolated by using the respective stack flow rates to yield a total for the two stacks. The emissions reported, as measured by the grab samples and the Orsat analysis, are a weighted average of the measurements made on both stack effluents.

Units F-1T, F-2T, F-3T and F-4T: TCC units F-1T and F-2T are twin units and TCC units F-3T and F-4T are twin units. Each unit is equipped with two stacks. Only one stack on each unit was sampled. Velocity traverses were made on both stacks of units F-1T and F-2T and on only one stack of units F-3T and F-4T. It was impossible because of the inaccessibility of sampling holes to measure the gas flow rate in both stacks of units F-3T and F-4T.

## TABLE V

### Operating Characteristics of Units Tested

| Unit Designation | Type | Date Tested | Feed Rate Fresh BPD | Feed Rate Recycle BPD | Catalyst Circulation Rate-Ton/Hr. | Regenerator Air Rate SCFM | Coke Burn-off Rate Lb./Hr. | Avg. Gas Temp. °F. |
|---|---|---|---|---|---|---|---|---|
| C-F | FCC | 8/30/56 | 24,000 | 0 | - | 22,200 | - | 520 |
| F-3T | TCC | 9/12/56 | 7,099 | 6,004 | 150 | 22,000 | 3,420 | 810 |
| F-4T | TCC | 9/12/56 | 6,053 | 6,013 | 120 | 23,000 | 3,000 | 710 |
| F-1T | TCC | 9/19/56 | 7,071 | 5,538 | 150 | 24,000 | 4,410 | 850 |
| F-2T | TCC | 9/19/56 | 6,506 | 5,602 | 150 | 25,000 | 5,020 | 740 |
| A-F | FCC | 10/4/56 | 40,000 | 10,000 | 4,500 | 112,000 | 38,000 | 820 |
| E-F | FCC | 10/9/56 | 25,000 | 9,000 | 3,240 | 64,000 | 21,600 | 530 |
| E-1T | TCC | 10/18/56 | 10,000 | 0 | 165 | 22,000 | 5,655 | 660 |
| E-2T | TCC | 10/18/56 | 8,000 | 3,000 | 150 | 27,600 | 4,620 | 610 |
| D-1T | TCC | 11/1/56 | 9,525 | 1,500 | 180 | - | 4,715 | 840 |
| D-2T | TCC | 11/1/56 | 8,525 | 7,400 | 150 | - | 2,610 | 700 |
| G-F | FCC | 11/8/56 | 6,462 | 606 | 390 | 13,300 | 5,400 | 610 |
| D-F | FCC | 11/27/56 | 32,610 | 13,680 | 2,532 | 97,500 | 36,416 | 485 |
| B-F | FCC | 12/4/56 | 29,500 | 2,045 | 1,560 | - | 23,100 | 510 |
| F-R | TCR | 12/13/56 | 13,940 | 50,000 gas SCFM | 42 | 16,200 | 1,700 | 480 |
| H-T | TCC | 12/19/56 | 6,500 | 3,000 | 166 | - | - | 680 |

Unit A-F: Three test runs were made on this unit. In the first, October 4, 1956, some of the samples were lost. The data presented in this paper are a combination of results of the three tests as follows:

| Date of Test | Substances Reported |
|---|---|
| October 4, 1956 | Hydrocarbons, aldehydes oxides of nitrogen |
| October 11, 1956 | Particulate, $SO_3$, $SO_2$, cyanides, $NH_3$ |
| October 17, 1956 | $CO_2$, $O_2$, CO, $N_2$ |

This unit is equipped with a flue gas heater located at the base of the stack.

Unit E-F: This catalytic cracking unit is equipped with an auxiliary unit which supplies heated air to the stack in order to reduce the visible plume. This air heater was not operating at the time of the test. The sampling point was below the inlet for the heated air.

Units D-1T and D-2T: These are twin TCC units, each equipped with a stack from its regenerator. The elevators carrying the regenerated and spent catalyst (one of each on each unit) are vented. A butterfly valve controls the effluent from these vents, allowing a portion of the effluent to be released to the atmosphere and sending the remainder to a Multiclone unit.

A full series of tests was carried out at the regenerator stack and the vent of the spent catalyst elevator, on one unit. The vent on the regenerated catalyst elevator on this same unit was sampled for particulate matter, $CO_2$, $O_2$, and CO. A full series of tests was also performed on the Multiclone unit stack.

Velocity determinations were made on the regenerator stack, the spent catalyst elevator vent and the regenerated catalyst elevator vent on the other unit.

The results of the test run on the one regenerator stack were used (by considering the relative velocities in both stacks) in the determination of the total emission rates. The losses from the elevator vents are presented at the end of this paper.

Unit D-F: This FCC unit is provided with two stacks. A full series of tests was run on both stacks. The results presented were obtained by combining the losses determined from each stack. This unit is equipped with a carbon monoxide boiler.

Unit B-F: This unit is also provided with two stacks. A full series of tests was run on both stacks. The results presented were obtained by combining the losses determined from each stack.

Unit F-R: It was decided to test this Thermofor Catalytic Reforming Unit, although it does not lie strictly with the scope of the program, because its operations are very similar to those of standard catalytic cracking units. The results of the tests on this unit are presented but these data are not considered in any discussion of the results as a whole or totaled with the other data to determine total emission figures.

## Studies of Sampling Methods

The primary object of this testing program is the determination of the nature and quantity of contaminants released to the atmosphere from catalytic cracker regenerator stacks. In hopes of obtaining information on the accuracy of the testing methods, a number of control tests were run:

Efficiency of Collection of Oxides of Sulfur:
A single weight Whatman thimble was set in the paper thimble train, following the impingers, to check the efficiency of the double weight Whatman thimble and the impingers for the collection of oxides of sulfur. Analytically, the single weight thimble was treated exactly as the double weight thimble. A number of determinations showed that no discernible amount of oxides of sulfur was captured by the single weight thimble.

Efficiency of Distilled Water in the Collection of Compounds of Ammonia.
The first impinger in the Alundum thimble train contains 100 ml. of distilled water, the second impinger contains 100 ml. of a 5% solution of HCl. The stack gases are acid and it has been the practice in previous tests to use distilled water in both impingers in belief that the water acidified by the stack gases would effectively collect ammonia and its compounds. In order to determine the effectiveness of distilled water in this setup,

for the collection of compounds of ammonia, an aliquot of the solution in the water impinger and the solution in the HCl impinger were filtered and evaporated to dryness (at 105°C) separately. The results of these determinations are shown in Table VI.

An average of 93.6% of the solids found after evaporation (for five units) of the impinger solution were captured in the first impinger. Unit F-R is excluded from this average since it is a TCR Unit; also, the small catch could result in an appreciable percentage error through slight analytical inaccuracies.

The water and HCl impinger solutions were analyzed separately for ammonia in three tests. The results reported as pounds per hour of $NH_3$ are as follows:

| Unit | $H_2O$ Impinger | HCl Impinger |
|---|---|---|
| H-T | 2.5 | 0.3 |
| B-F North Stack | 18 | 0 |
| B-F South Stack | 8.3 | 0.4 |

The distilled water in the first impinger was acidified by the stack gases and acted as an efficient, though not proven quantitative, collector of ammonia and its compounds.

In calculating the total particulate matter emitted, the weight of insoluble solids in the water and HCl impinger solution was added to the alundum thimble catch. It is not known whether any of the solids found on evaporation of the impinger solutions would actually condense from the stack gases emitted to the atmosphere. It is believed this residue is composed mainly of compounds of ammonia (sulfates and sulfites). It should be noted that the results, reported as "Lbs./Hr. - Residue on Evaporation to Dryness", have no definite significance when considering the character of particulate matter in the stack emissions.

## Particulate Matter:

The particulate matter in the flue gas is determined, as discussed above, by adding the alundum thimble catch and the insoluble material (obtained by filtration) caught in the impingers of the alundum thimble train.

TABLE VI

Insoluble Solids and Residue on Evaporation
To Dryness in $H_2O$ and HCl Impinger Solutions

| Unit Tested | $H_2O$ Impinger | | HCl Impinger | | Total Residue in Both Impingers on Evaporation to Dryness Lbs. /Hr. |
|---|---|---|---|---|---|
| | Insoluble Solids Lbs. /Hr. | Residue on Evaporation to Dryness Lbs. /Hr. | Insoluble Solids Lbs. /Hr. | Residue on Evaporation to Dryness Lbs. /Hr. | |
| C-F | 4.77 | - | 2.89 | - | - |
| F-3T | 5.28 | - | 1.72 | - | - |
| F-4T | 1.55 | - | 1.36 | - | - |
| F-1T | 0.19 | - | 0.19 | - | - |
| F-2T | 0.89 | - | 0.17 | - | - |
| E-F | 11.9 | - | 1.3 | - | 325 |
| E-1T | 2.86 | - | 1.15 | - | 25.2 |
| E-2T | 3.60 | - | 0.03 | - | 18.3 |
| A-F | 4.16 | - | 1.6 | - | 471 |
| D-1T | 0.24 | - | 0.04 | - | 3.23 |
| D-2T | - | - | - | - | - |
| G-F | 1.78 | - | 0.19 | - | 85.9 |
| D-F | 4.1 | 39.1 | 0.42 | 5.1 | 44.2 |
| | 3.49 | 77.8 | 0.55 | 4.8 | 82.6 |
| B-F | 1.5 | 118 | 0.54 | 0.85 | 119 |
| | 1.2 | 70.3 | 0.31 | 2.3 | 72.6 |
| F-R | 0.24 | 0.88 | 0.24 | 1.09 | 1.97 |
| H-T | 0.22 | 9.73 | 0.01 | 1.15 | 10.88 |

TABLE VII

Particulate Matter

| Unit | Total Particulate Lbs/Hr. | Unit | Total Particulate Lbs/Hr. |
|---|---|---|---|
| C-F | 181 | E-2T | 8.06 |
| F-3T | 9.53 | D-1T | 1.36 |
| F-4T | 10.01 | D-2T | 1.64 |
| F-1T | 3.44 | G-F | 6.42 |
| F-2T | 2.22 | D-F | 58.7 |
| A-F | 57.5 | B-F | 61.0 |
| E-F | 28.3 | F-R | 17.8 |
| E-1T | 13.8 | H-T | 4.3 |

Some of the results in Table VII were determined by testing one stack of two similar units or one stack of a unit with two stacks and extrapolating the results according to respective velocities (see description of units at the beginning of this section).

Per cent Loss on Ignition:

The alundum thimble, after having been weighed for the determination of the particulate catch, is placed in a furnace whose temperature is raised to 1000°F. and maintained at that temperature for one-half hour. The resultant loss in weight (listed as per cent loss on ignition) is shown in Table VIII. This is the per cent loss in weight of the thimble catch only. The thimble catch calculated in pounds per hour is also shown on Table VIII. To obtain the total particulate matter discharged from the stack (see Table VII) the weight of the insoluble solids filtered from the $H_2O$ and HCl solutions are added to the weight of the alundum catch before ignition. The major portion of the unvolatilized material is probably composed of catalyst dust.

## TABLE VIII

### Percent Loss of Particulate Matter on Ignition

| Unit Tested | Alundum Thimble Catch - Lbs/Hr. | % Loss on Ignition (1000°F) |
|---|---|---|
| C-F | 173 | 73 |
| F-3T | 2.33 | 63 |
| F-4T | 7.1 | 64 |
| F-1T | 3.06 | 66 |
| F-2T | 1.16 | 96 |
| E-F | 15.1 | 45 |
| E-1T | 9.79 | 56 |
| E-2T | 4.43 | 58 |
| A-F | 51.7 | 64 |
| D-1T | 1.08 | 58 |
| D-2T | - | - |
| G-F | 4.45 | 56 |
| D-F | 28.4 | 30 |
| | 21.8 | 41 |
| B-F | 29.4 | 63 |
| | 28.1 | 44 |
| F-R | 17.3 | 14 |
| H-T | 4.07 | 59 |

It is conceivable that the percentage of particulate matter lost on ignition could vary, depending upon the method of collection; that is, if it is necessary to keep the thimble holder within the stack during the test (in order to maintain within the holder a temperature above the dew point of the stack gases) some of the volatile material might not be collected. The temperatures of the gases in the various regenerator stacks varied between 480-840°F. The average sample point temperature in the stack was approximately 630°F. The temperature of the gases within the thimble holder was not measured but it was obviously lower than what it would have been if the thimble had been placed within the stack. The thimbles were insulated with asbestos cloth and inspected after the tests were completed, to be sure that no condensation occurred. During the tests, the tubing connecting the outlet of the thimble holders and the impinger inlets were inspected for condensate. No condensate was observed.

Location of Alundum Thimble:

In placing the alundum thimble holder outside the stack during the sampling period the following factors were considered:

1. It was possible to maintain the temperature of the gases within the thimble holder above the dew point of the stack gases by proper insulation and thus effect dry collection with the thimble placed outside the stack.

2. The gasket (one-eighth inch thick silicone rubber laminated with glass fiber) used in the alundum thimble holder is not effective at temperatures above 500°F.

3. Placing the thimble outside the stack maintains conditions within the holder which approach the conditions at the point of discharge more closely than placing the thimble within the stack.

Hydrocarbons:

The mass spectrometer (M. S. ) and infrared spectrophotometer (I. R. ) procedures are presented in the Appendix. A thorough understanding of these procedures is necessary in order to recognize the limitations of the analytical methods.

The M. S. and I. R. results are presented in Table IX. No direct correlation is evident between the concentrations of hydrocarbons as determined by the two different analytical methods.

TABLE IX

Total Hydrocarbon Emissions

| Unit | Mass Spectrometer | | | | Infrared Spectrophotometer | |
|---|---|---|---|---|---|---|
| | Hydrocarbons Tons/Day | Hydrocarbons ppm | Wt. % $C_1$ & $C_2$ | Vol. % $C_1$ & $C_2$ | Hydrocarbons (as Hexane) Tons/Day | Hydrocarbons (as Hexane) ppm |
| C-F | 2.1 | 760 | 68.3 | 85.5 | 0.6 | 65 |
| F-3T (1) F-4T (1) | 0.5 | 121 | 67.4 | 67.8 | - (5) | - |
| F-1T (1)(2) F-2T (1)(2) | 0.1 | 87 | 79.5 | 77 | 0.02 - (6) | 9 - |
| A-F (3) | 7.4 | 1213 | 67.7 | 87.4 | 0.02 | 14 |
| E-F (3)(4) | - | - | - | - | 2.8 | 142 |
| E-1T (3) | 0.4 | 308 | 40.9 | 70.8 | 1.2 | 116 |
| E-2T (3) | 0.5 | 484 | 55.1 | 81.4 | 0.04 | 13 |
| D-1T (4) | - | - | - | - | 0.15 | 43 |
| D-2T (4) | - | - | - | - | 0.02 | 8 |
| G-F (3) | 0.3 | 328 | 51.2 | 75.3 | 0.02 (7) | - |
| D-F (2) | 1.0 | 98 | 42.3 | 54.1 | - | Trace |
| B-F | 3.1 | 1150 | 84.1 | 94.6 | 0.3 | 12 |
| F-R (2) | 0.1 | 88 | 45.4 | 65.9 | 0.89 | 78 |
| H-T | 1.4 | 1655 | 61.9 | 18.8 | 0.03 | 8 |
| | | | | | 0.30 | 108 |

Note: All concentrations are reported on a dry basis.

(1) Only the mass spectrometer results for units F-2T and F-4T were reliable. Since units F-1T and F-2T and units F-3T and F-4T are twin units, the data shown result from combining the twin units, using the mass spectrometer data for units F-2T and F-4T.

(2) No methane present as determined by mass spectrometer.

(3) Mass spectrometer determinations include oxygenated $C_4$ and $C_5$ hydrocarbons.

(4) The mass spectrometer results were not reliable.

(5) The infrared spectrophotometer results were not reliable.

(6) Concentration of hydrocarbons is below limit of accuracy of the infrared spectrophotometer.

(7) Infrared spectrophotometric determinations were made on unit D-1T only. The result shown is obtained by assuming that twin units D-1T and D-2T emit the same quantity of hydrocarbons.

The M S. results indicate that a large percentage of the hydrocarbons found lies within the $C_1$ and $C_2$ range. This fact may be used to account for the discrepancy between the M. S and I. R. results.

In the I R. analytical method, as outlined in the Appendix, the absorbance is measured at approximately 3. 45 microns. Absorbance at this wave length is attributed to the carbon-hydrogen stretching bond. The I. R instrument used in this series of tests is calibrated against n-hexane and all results are expressed in terms of n-hexane. This is an expedient employed, mainly for general atmospheric sampling, to standardize results and facilitate analysis.

It is obvious that when analyzing for hydrocarbons by the I. R. method outlined in the Appendix and reporting the results as hexane, a number of discrepancies arises. For each type of hydrocarbon there is an increase in absorbance with molecular weight. Paraffinic hydrocarbons contribute to a greater extent to the measurement than do the olefins. Acetylenic compounds and aromatics are exceptionally weak contributors.

Using the I. R. calibrated for hexane, 100 ml. of methane would have an absorbance equal to 1 ml. of hexane and approximately 5 ml. of ethane would appear as 1 ml. of hexane. This accounts for the fact that the concentration of hydrocarbons as determined by I. R was less than that as determined by M. S. I. R. determinations were made because considerable work has been done by this method in the past. In this report the M. S. results are used for reporting total hydrocarbon emissions since these appear to be more reliable.

The outstanding characteristic of mass spectrometric analysis of stack gases is the determination of the distribution of hydrocarbons by molecular weight. The accuracy of the values obtained by this method, however, is limited by two factors. The first is the lack of knowledge of the isomeric distribution of the hydrocarbons in the stack gas at each molecular weight. For maximum accuracy, calibration data of hydrocarbons used in the calculation should be weighted at each molecular weight in the same proportions as the isomeric distribution of the corresponding hydrocarbons. Since the isomeric distribution of the hydrocarbons in the stack gas is not known, best weightings of the calibration data cannot be made. The weightings used hence introduce some error into the calculations, although the error is probably not large.

The second factor is the presence of non-hydrocarbons, both organic and inorganic, which have the same molecular weight as the hydrocarbons in the stack gas. In many cases, the presence of these compounds cannot be

recognized. Hence calculated hydrocarbon values may be high, by the amount of non-hydrocarbon contribution to the hydrocarbon peak. Because of the preceding two sources of error, numerical values calculated for hydrocarbons with the exception of methane, should be considered as indicating approximate magnitudes rather than exact amounts.

Organic non-hydrocarbons are very difficult to recognize in the presence of relatively large quantities of hydrocarbon and correspondingly difficult to determine. In general, no calculation is made for these classes of materials. However, inorganic compounds are generally easily recognized and determined. The accuracy of calculation of this type is good.

Sulfur Oxides, Ammonia, Cyanides, Aldehydes, Oxides of Nitrogen, $CO_2$, $O_2$, and CO:

The results of the determinations for sulfur oxides, ammonia and cyanides are shown on Table X. Aldehydes, oxides of nitrogen, $CO_2$, $O_2$, CO and $N_2$ are shown on Table XI.

Where possible, comparison is made between the results obtained by chemical and infrared spectrophotometric analysis and those obtained by mass spectrometer analysis. All concentrations are shown on a dry basis so that the above comparison may be made.

The percentage moisture in the stack gas samples as determined by measuring the condensate in the impingers (average of both trains) and as determined in the mass spectrometer are shown in Table XII. The rates of flow of flue gases on a wet and dry basis are also presented.

The concentration of water vapor as determined by the mass spectrometer is not the same as that in the stack gas at stack conditions. On cooling from stack temperature, considerable water condenses in the sample container. The concentration reported is that in the gas phase of the sample when admitted into the mass spectrometer.

Reproduced from best available copy.

## TABLE X

Sulfur Oxides, Ammonia, and Cyanides

| Unit | $SO_3$ Lbs/Hr. | $SO_2$ Chem. Lbs/Hr. | $SO_2$ Anal. PPM | $SO_2$ M. S. PPM | Total S as $SO_2$ Vol. % | Wt. % $SO_3$ in total Oxides of Sulfur | $NH_3$ Lbs/Hr. | $NH_3$ PPM | Cyanides as HCN Chem. Lbs/Hr. | Cyanides as HCN Anal. PPM | Cyanides as HCN M. S. PPM |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C-F | 1.2 | 1260 | 2190 | 1850 | 0.22 | 0.1 | 20.5 | 134 | trace | trace | 240 |
| F-3T | 5.74 | 13.0 | 105 | - | 0.015 | 30.6 | 1.56 | 47 | trace | trace | - |
| F-4T | 7.77 | 11.1 | 97 | 60 | 0.015 | 41.2 | 3.12 | 103 | trace | trace | 180 |
| F-1T | 1.6 | 18.7 | 151 | - | 0.016 | 7.9 | 2.2 | 67 | trace | trace | - |
| F-2T | 2.7 | 13.2 | 136 | 91 | 0.016 | 17.0 | 1.9 | 74 | trace | trace | 90 |
| A-F | 164 | 535 | 438 | 47 | 0.055 | 23.5 | 130 | 401 | 0.25 | 0.48 | 430 |
| E-F | 6.9 | 648 | 984 | - | 0.098 | 1.1 | 118 | 675 | 0.054 | 0.19 | - |
| E-1T | 5.1 | 15.1 | 86.2 | 15 | 0.011 | 25 | 4.6 | 99 | 0.005 | 0.07 | 370 |
| E-2T | 2.0 | 14 | 65 | 10 | 0.008 | 13 | 3.4 | 60 | 0.06 | 0.7 | 230 |
| D-1T | 1.25 | 17.5 | 114 | - | 0.011 | 6.7 | 1.2 | 29 | 0.01 | 0.15 | - |
| D-2T | - | - | - | - | - | - | - | - | - | - | - |
| G-F | 3.07 | 205 | 1310 | 360 | 0.13 | 1.4 | 23 | 550 | 0.018 | 0.27 | 190 |
| D-F | 8.9 | 453 | 308 | 20 | 0.031 | 1.8 | 26 | 67 | 0.291 | 0.47 | 170 |
| B-F | 12 | 362 | 512 | 220 | 0.054 | 3.2 | 27 | 140 | 0.28 | 0.94 | 360 |
| F-R | 0 | 0.8 | 4.1 | 30 | - | 0 | 0 | 0 | 0.024 | 0.31 | 120 |
| H-T | 0.62 | 24.4 | 141 | 15 | 0.014 | 2.5 | 2.8 | 61 | 0.039 | 0.54 | 220 |

Note: All concentrations are reported on a dry basis.

TABLE XI

Aldehydes, Oxides of Nitrogen, $CO_2$, $O_2$, CO, and $N_2$

| Unit | Aldehydes as HCHO | | $NO_x$ as $NO_2$ | | NO by M.S. | $CO_2$, Vol. % | | $O_2$, Vol. % | | CO, Vol. % | $N_2$, Vol. % by Difference |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Lbs/Hr. | PPM | Lbs/Hr. | PPM | PPM | Orsat | M. S. | Orsat | M. S. | Orsat | Orsat |
| C-F | 25.9 | 96 | 163 | 394 | 150 | 10.0 | 11.8 | 2.3 | 2.3 | 6.1 | 81.6 |
| F-3T | 2.6 | 44 | 2.7 | 30 | - | 8.4 | - | 9.8 | - | 0 | 81.6 |
| F-4T | 3.4 | 63 | 0.6 | 7 | 130 | 8.8 | 9.2 | 7.8 | 11.1 | 2.6 | 80.8 |
| F-1T | 0.6 | 12 | 3.1 | 34 | - | 9.6 | - | 8.3 | - | 1.5 | 80.6 |
| F-2T | 0.4 | 9 | 2.2 | 32 | 190 | 12.8 | 13.3 | 2.5 | 2.5 | 3.6 | 81.1 |
| A-F | 77 | 130 | 26 | 29 | 250 | 8.7 | 11.1 | 5.1 | 2.2 | 4.9 | 81.3 |
| E-F | 0.9 | 3 | 5.9 | 12 | - | 9.5 | - | 2.7 | - | 6.8 | 81.0 |
| E-1T | 2.2 | 26 | 0 | 0 | 200 | 9.2 | 12.1 | 6.6 | - | 3.2 | 81.0 |
| E-2T | 1.2 | 12 | 0 | 0 | 170 | 4.7 | 9.0 | 13.5 | - | 0.7 | 81.1 |
| D-1T | 3.5 | 49 | 5.7 | 51 | - | 8.2 | - | 7.9 | - | 1.4 | 82.5 |
| D-2T | - | - | - | - | - | - | - | - | - | - | - |
| G-F | 1.5 | 20 | - | - | 310 | 7.8 | 7.8 | 5.1 | 5.5 | 6.1 | 81.0 |
| D-F | 4 | 5 | 202 | 191 | 11 | 13.4 | 13.4 | 2.0 | 2.3 | 0 | 84.6 |
| B-F | 18 | 53 | 4.2 | 8.3 | - | 8.5 | 8.8 | 3.5 | 4.1 | 7.8 | 80.2 |
| F-R | 0.5 | 5 | 3.2 | 23 | 75 | 5.2 | 3.9 | 14.3 | 13.1 | 0 | 80.5 |
| H-T | 14.3 | 177 | 7.7 | 62 | 230 | 9.0 | 9.0 | 6.9 | 7.3 | 4.1 | 80.0 |

Note: All Concentrations are reported on a dry basis.

## TABLE XII

### Per cent Moisture and Flue Gas Volumes

| Unit | Vol. % $H_2O$ as Determined from Sampling Trains | Vol. % $H_2O$ in M.S. Sample | Rate of Flow of Flue Gases SCFM (Wet Basis) | Rate of Flow of Flue Gases SCFM (Dry Basis) |
|---|---|---|---|---|
| C-F | 26.3 | 0.186 | 77,200 | 56,900 |
| F-3T | 11 | - | 13,800 | 12,300 |
| F-4T | 11 | 0.600 | 12,700 | 11,300 |
| F-1T | 12.2 | - | 13,970 | 12,270 |
| F-2T | 19 | 0.885 | 11,860 | 9,600 |
| A-F | 19.7 | 0.480 | 151,000 | 121,300 |
| E-F | 18 | - | 80,900 | 65,000 |
| E-1T | 16.5 | 0.626 | 20,700 | 17,280 |
| E-2T | 11.1 | 2.448 | 23,600 | 20,980 |
| D-1T | 12.1 | - | 17,300 | 15,200 |
| D-2T | - | - | 20,800 | - |
| G-F | 25.3 | 0.458 | 20,800 | 15,540 |
| D-F | 18.7 | 0.229 | 178,800 | 145,400 |
| B-F | 19.2 | 0.47 | 86,300 | 69,700 |
| F-R | 4.3 | 0.22 | 19,000 | 18,200 |
| H-T | 7.5 | 1.762 | 18,400 | 17,000 |

The concentration of $H_2O$ as determined from condensate in the impingers of the sampling trains is reported at stack conditions. The increase in volume of the impinger solutions is measured, and using the temperature and pressure at the impingers and assuming the gases going through the meter are saturated with water vapor, the percentage moisture in the stack gas is calculated.

The data presented in Table XII above should be used if it is desired to convert the reported concentrations (Tables X and XI) to a wet basis.

## Organic Acids:

Organic acids were determined by the standard method used by the Los Angeles Air Pollution Control District. During the testing program a number of discrepancies were noted in the reported results. It was found that the standard method for this determination could not be employed in this series of tests. The sulfur dioxide present in the stack gases interfered by being extracted as $H_2SO_3$ by the ether during analysis. It was further discovered that all the organic acids collected in the caustic may not have been completely extracted before titration.

The testing program was completed before the analytical procedure could be corrected, thus the organic acid results are not reported. The revised method for the analysis is presented in the Appendix-(method 3) as a tentative procedure.

## Catalyst Elevator Vents:

TCC Units D-1T and D-2T employ bucket bype elevators to transfer the regenerated and fresh catalyst to the reactor, and spent catalyst to the regenerator. As noted in the description of the units, these elevators are enclosed and provided with vents discharging directly to the atmosphere. A portion of the effluent being released through the two spent catalyst vents is passed through cyclone collectors.

Tests were made in the spent catalyst elevator vent stack, the fresh catalyst elevator vent stack and the outlet stack of the multiclone.

The results of these tests are presented in Table XIII and give an indication of the substances that are emitted if elevator enclosures leak or if elevator vents are not provided with proper controls.

## TABLE XIII

### Emissions from TCC Elevator Stacks

| | Unit D-1T | | Unit D-2T | | D-1T and D-2T |
|---|---|---|---|---|---|
| | Spent Catalyst Vent | Fresh Catalyst Vent | Spent Catalyst Vent | Fresh Catalyst Vent | Multiclone Outlet |
| SCFM | 260 | 330 | 240 | Negligible | 3,740 |
| Particulate Matter - lbs/hr. | 2.4 | 0.6 | -- | -- | 33 |
| $SO_3$ - lbs/hr. | 0.02 | -- | -- | -- | 0.2 |
| $SO_2$ - lbs/hr. | 0.08 | -- | -- | -- | 1.28 |
| Cyanides (as HCN) lbs/hr. | 0.0004 | -- | -- | -- | 0.002 |
| $NH_3$ - lbs/hr. | 0.06 | 0.002 | -- | -- | 0.35 |
| Hydrocarbons (as $C_6H_{14}$)-ppm | 172 | -- | -- | -- | 95 |
| Aldehydes - ppm (as HCHO) | 73 | -- | -- | -- | 44 |
| $NO_x$ as $NO_2$ - ppm | 5 | -- | -- | -- | 5 |
| $H_2O$ - Vol. % | 42.7 | 3 | -- | -- | 28.8 |
| $CO_2$ - Vol. % | 1.6 | 1.6 | -- | -- | 0.8 |
| $O_2$ - Vol. % | 16.1 | 19.6 | -- | -- | 19 |
| CO - Vol. % | 0.0 | 0.0 | -- | -- | 0.0 |
| $N_2$ - Vol. % | 82.3 | 78.8 | -- | -- | 80.2 |

Note: All concentrations are shown at stack conditions (wet basis).

## TOTALS AND SUMMATION

The total figures presented in Table XIV should not be considered as absolute values. They represent the total of specific emission rates, of all catalytic cracking unit regenerator stacks tested at various times over a three-months' period. The operating conditions of these units change from time to time and thus the quantity and character of the material emitted may vary. All the data presented in this paper (including the totals shown in Table XIV) should be considered to represent ranges.

Not all the units were tested for all the substances originally scheduled for determination. Interpolated and extrapolated results were sometimes employed to obtain a value which might represent an actual emission rate. Therefore, it is important that the text be consulted when examining Table XIV.

Table XIV is presented to give an indication of the relative amounts of certain substances emitted from catalytic cracking unit regenerator stacks. No inference is intended as to the extent these substances contribute to air pollution or controls that may be needed.

It should be noted from an examination of the data presented in Tables X and XI that in some instances a major portion of the emissions of specific substances is produced by relatively few units.

TABLE XIV

Total Emission Rates from Catalytic Cracker Regenerator Stacks

| Substance | Rate |
|---|---|
| Particulate Matter(1) | 5.4 tons/day |
| Sulfur Trioxide(1) | 2.7 tons/day |
| Sulfur Dioxide(1) | 48.3 tons/day |
| Ammonia(1) | 4.4 tons/day |
| Cyanides (as HCN)(1) | 24.0 lbs./day |
| Aldehydes (as HCHO)(1) | 1.9 tons/day |
| Oxides of Nitrogen (as $NO_2$)(1) | 5.2 tons/day |
| Hydrocarbons (2)(3) | 20 tons/day |

NOTE: The above totals do not include Unit F-R (the Thermofor Catalytic Reforming Unit)

(1) as determined by physical and chemical analysis.

(2) as determined by mass spectrometric analysis.

(3) The sum of the emission rates shown in Table IX is 16.9 Tons of Hydrocarbons per day. This total does not include the hydrocarbon emission rates of units E-F, D-1T and D-2T. The rate of 20 tons per day shown in Table XIV was arrived at by estimating the hydrocarbon emission rates of units E-F, D-1T and D-2T by using data obtained from tests of similar units.

## APPENDIX

## Analytical Procedures

### Table of Contents


| | | Page |
|---|---|---|
| 1. | Analytical Procedure for Ammonia | 35 |
| 2. | Analytical Procedure for Oxides of Sulfur | 36 |
| 3. | Analytical Procedure for Organic Acids (Tentative) | 36 |
| 4. | Analytical Procedure for Cyanides | 39 |
| 5. | Analytical Procedure for Aldehydes | 42 |
| 6. | Analytical Procedure for Oxides of Nitrogen (Phenoldisulfonic Acid Method) | 44 |
| 7. | Infrared Spectrophotometric Method for Determination of Hydrocarbons | 46 |
| 8. | Analysis of Stack Gases By Mass Spectrometer | 46 |

## 1 Analytical Procedure for Ammonia*

### Reagents

30 per cent sodium hydroxide solution
Standard 0.1N sulfuric acid solution
Standard 0.02N sodium hydroxide solution
Methyl red indicator solution

### Procedure

Combine the filtered solutions from the three impingers from the water-HCl sampling train and note the volume. Dilute a 50 ml. aliquot of the sample to approximately 250 ml. in a 500 ml. Kjeldahl flask. Add a few glass beads or boiling pellets to prevent bumping of the solution. Add 25 ml. of 30 per cent sodium hydroxide solution and quickly connect the flask to a Kjeldahl distilling rack.

Distil 100-150 ml. of the solution into a 500 ml. Erlenmeyer flask containing an excess (100 ml.) of 0.1N sulfuric acid. The delivery tube must dip below the surface of the 0.1N sulfuric acid, and care must be taken to prevent the solution from "sucking back" into the Kjeldahl flask.

Titrate the excess sulfuric acid with 0.02N sodium hydroxide, using four drops of methyl red as an indicator.

### Calculations

$$\text{grams of ammonia collected in train} = \frac{(100\,N_1 - V_3N_2)(V_1)(0.017)}{(V_2)}$$

Where $N_1$ = normality of sulfuric acid solution

$N_2$ = normality of sodium hydroxide solution

$V_1$ = total volume of solution in impingers

$V_2$ = volume of aliquot taken for analysis

$V_3$ = volume of sodium hydroxide solution used in titration of excess sulfuric acid

NOTE
The amount of solution taken as an aliquot may be varied, depending upon the concentration of ammonia present. Results are reported to the nearest 0.5 mg.

---

* Scott, "Standard Methods of Chemical Analysis," 5th Edition, Vol. I, pp. 637-638

## 2 Analytical Procedure for Oxides of Sulfur

### Reagents

Bromine water
Concentrated hydrochloric acid
10 per cent barium chloride solution
Silver nitrate solution

### Procedure

Dilute a 100 ml. aliquot of the combined impinger solutions from the 5 per cent sodium hydroxide sampling train to 200 ml. Add bromine water in slight excess (until color remains) to oxidize the $SO_2$. Boil until the solution is colorless and continue boiling for another five minutes to expel the excess bromine. Neutralize with concentrated hydrochloric acid and add 2 ml. excess. Filter if necessary to remove any silica or other solid material. Heat to boiling and add 10 per cent barium chloride solution with constant stirring until an excess is present. Digest the solution for one hour over a steam bath. Filter through a fine ashless filter paper, checking the filtrate for complete precipitation. Wash with hot water until the filtrate is free of chloride as determined by adding silver nitrate solution to the washings. Transfer the paper and precipitate to a tared crucible, dry and ignite to constant weight at 750°C.

The water extract of sulfur trioxide from the Whatman thimbles is determined as above with the exception that bromine oxidation is omitted.

### NOTE

Results are reported to the nearest 0.2 mg.

## 3 Analytical Procedure for Organic Acids (Tentative)

### Principles

Organic acids from atmospheric or industrial gas samples may be collected by absorption in a five per cent sodium hydroxide solution. A continuous flow impinger train has been found to be an efficient absorbing apparatus.

The alkaline absorbing solution is subsequently rendered acidic and the liberated organic acids extracted with ether and determined by titration with standard alkali.

Reagents; 0.1N NaOH; Phenolphthalein indicator; Sulfuric acid, reagent grade.

Equipment

Liquid-liquid extraction apparatus, medium size, as Corning No. 92232 or equivalent.

Glas-col 500 ml. mantle and rheostat.

Precedure

The sodium hydroxide absorbing solution is quantitatively transferred from the impingers to a 600 ml. beaker. Small distilled water rinses should be used to effect this transfer, keeping the volume as small as possible. The beaker is placed in an ice bath and allowed to come to temperature equilibrium after which it is covered with peroxide and acid-free ethyl ether(1).

Concentrated sulfuric acid(2) is added dropwise to the beaker with constant stirring until a pH of 2.0 is attained as determined with an external indicator, preferably a pH meter.

The acidulated absorbing solution is then transferred to a liquid-liquid extractor. The transfer is facilitated with the aid of a long stemmed funnel(3) which serves to introduce the sample into the extractor without permitting droplets to occur in the side arm, etc. The final level of the aqueous layer should be approximately two inches below the level of the side arm. The inner tube of the extractor is lowered into position and a 500 ml. short-neck round bottom flask containing approximately 250 ml. ether and an ebulator is attached to the side arm.

Organic Acids Determination

The apparatus is then placed in the hood, fastened in place with a heating mantle under the flask and the reflux condenser connected. The ether flask is heated in the mantle so that vigorous boiling is attained and ether is being condensed rapidly, dropwise, from the reflux condenser into the inner extractor tube(4).

The extraction is continued for a total of eight hours(5).

After the elapsed extraction time, the apparatus is allowed to cool and the condenser removed. The entire apparatus is tilted to permit most

of the ether layer in the extractor to flow into the flask. Care must be exercised to prevent any of the aqueous layer from also flowing into the flask.

The flask is disconnected, the ebulator removed and the contents transferred to a separatory funnel. It will be noted that a small aqueous portion is present in the ether(6). This portion is carefully drained off and discarded. Approximately 40 ml. of distilled water plus three drops of phenolphthalein are added to the separatory funnel.

The solution is titrated in the funnel with 0.1N NaOH until, after vigorous shaking, a pink color persists.

A blank determination is performed in exactly the same manner, a portion of the prepared impinger solution being retained, acidulated, extracted, etc., for this purpose. The reagent blank determination must be performed.

Notes:

(1) The ether layer is present to avoid loss of organic acids liberated at the point of contact. There is also a vigorous evolution of $CO_2$ which may otherwise carry off some acids.

(2) Concentrated acid is used in order to maintain a small working volume.

(3) A long stem funnel is easily constructed using a conventionnal funnel to which is attached a suitable length of tygon tubing.

(4) If boiling should appear to cease during the refluxing period, the flask should be permitted to cool somewhat, after which gentle tapping will restore boiling. Following the gentle tapping, the heat should be reapplied at the same or slightly higher temperature.

(5) It has been observed that at a rapid refluxing rate, about 85 liters of ether will pass through the apparatus during eight hours.

(6) A small volume of water will collect in the flask due to the high solubility of water in ethyl ether. Ethyl ether is used in the method, however, because when the extraction is performed at pH 2.0, phenolic compounds will not be extracted.

Calculations:

The blank titration(ml.) is deducted from the sample titration.

Calculations are normally based upon acetic acid values, hence:

(ml. NaOH) (N) (0.06) = gms. acetic acid,

which value may subsequently be related to total gas sample and calculated as ppm.

## 4 Analytical Procedure for Cyanides*

### Reagents

15 per cent hydrochloric acid solution
Saturated lead acetate solution
1 per cent picric acid solution. Commercial picric acid usually contains about 10 per cent water, and this must be considered when the solution is made up.
Potassium dichromate crystals
Standard potassium cyanide solution equivalent to 100 mg. HCN per liter (standardized)
Sodium carbonate solutions; 0.25 molar, 0.5 molar, and 1 molar
10 per cent sodium hydroxide solution
15 per cent sulfuric acid solution
Methyl red indicator

### Procedure

A 100 ml. aliquot of the stack sample (absorbed in 5 per cent sodium hydroxide solution) is transferred to the flask of a distillation apparatus as illustrated in Fig. 765.1, API Manual on Disposal of Refinery Wastes, Volume V. Volatile reducing agents, notably sulfites and sulfides, interfere with the determination, so the absorber solution must be tested for the presence of these substances as follows:

Sulfides: Test the absorber solution by placing a drop on lead acetate test paper or by some equivalent method. If sulfides are present, proceed as described under "Sulfides Present."

* "Determination of Hydrogen Cyanide and Cyanogen," Colorimetric Methods, API Method 765-54, Manual on Disposal of Refinery Wastes, Vol. V., "Sampling and Analysis of Waste Gases and Particulate Matter," first Edition.

Sulfites: Mix a drop of 10 per cent potassium ferrocyanide solution, a drop of cold saturated zinc sulfate or zinc nitrate solution, and a drop of 1 per cent sodium nitroprusside solution. A white precipitate of zinc ferrocyanide is formed. To this add a drop of neutralized absorber solution. If the precipitate develops a red color, sulfites are present. In this case proceed as described under "Sulfites Present."

A. No sulfides or sulfites present: Add a few drops of methyl red indicator solution to the solution in the distillation flask and connect the flask to the distillation apparatus.

Immerse the sintered glass tip of the condenser tube in 25 ml. of 1 molar sodium carbonate solution contained in a 100 ml. graduated cylinder. Apply a low flame to the distillation flask, and when boiling has started, pass steam through the system. When reflux has started and back pressure has caused the carbonate solution to rise slightly in the condenser tube, add slowly from the dropping funnel 15 per cent sulfuric acid until the sample is distinctly acidic to methyl red indicator. If the sample contains a large amount of carbonate or bicarbonate, large quantities of carbon dioxide will excape from the system. This evolution will cease when the methyl red indicator changes color, and again the rapid condensation of the steam will cause a back pressure in the system and the carbonate solution in the cylinder to rise slightly. This back pressure should be maintained throughout the remainder of the distillation. Negligible hydrogen cyanide is lost during the evolution of carbon dioxide.

When the distillate volume has reached about 75 ml., lower the receiving graduate and increase the heat to the distillation flask to provide for a thorough washdown of the inside of the condenser by the condensate. Wash down the outside of the condenser and stop the distillation.

Transfer this distillate to a 100 ml. volumetric flask and dilute to volume with distilled water. Pipette a 10 ml. $\pm$ 0.01 ml. aliquot into a dry 100 ml. volumetric flask and add 5 ml. $\pm$ 0.01 ml. of the picric acid solution. Develop the color by immersing the flask in boiling water for 5 min. $\pm$ 0.5 min. Remove and fill almost to the mark, cool to room temperature, and fill exactly to the mark.

Observe the absorption at 520 mμ against distilled water in a photometer. If the absorption is greater than that covered by the standard curve, transfer a smaller aliquot portion of the distillate to a 100 ml.

volumetric flask and add sufficient 0.25 molar sodium carbonate solution to bring the volume to 10 ml. ± 0.01 ml. Then add 5 ml. ± 0.01 ml. of picric acid and repeat as outlined hereinbefore.

B. Sulfites Present: Add a large excess of potassium dichromate crystals (1 g. is usually sufficient) to the absorber solution in the distillation flask to oxidize all sulfites present. Add a few drops of methyl red indicator solution, attach the flask to the distillation apparatus, and proceed as described in A, "No sulfides or sulfites present."

C. Sulfides Present: After placing the absorber solution in the distillation flask, cool the flask in an ice bath and titrate the solution to a pH of 2 with a glass electrode or indicating paper using 15 per cent hydrochloric acid solution. Add enough saturated lead acetate solution to precipitate all of the sulfide present, and then add 2 ml. in excess. Stopper the flask and shake vigorously to insure the removal of any hydrogen sulfide above the solution.

Attach the flask to the distillation assembly and pass steam into the cold solution. Continue the distillation as described in A, "No sulfides or sulfites present," omitting the addition of sulfuric acid. Test a portion of the distillate for sulfide with a drop of lead acetate solution. If the test is positive, either the sulfide precipitation is incomplete or the pH of the solution is too low. Repeat the procedure on a fresh portion of the sample, making appropriate corrections.

## Preparation of Standard Curve

Pipette 10, 20, 50, and 100 ml. portions of the standard potassium cyanide solution into separate 100 ml. volumetric flasks and dilute each to volume with distilled water.

Pipette a 5 ml. ± 0.01 ml. aliquot from each flask into dry 100 ml. volumetric flasks. Prepare a blank by pipetting 5 ml. ± 0.01 ml. of distilled water into a fifth volumetric flask. To each of the 5 flasks add 5 ml. ± 0.01 ml. of the 0.5 molar sodium carbonate solution and 5 ml. ± 0.01 ml. of the 1 per cent picric acid solution, in that order.

Immediately immerse the flasks in boiling water for 5 min. ± 30 sec. Remove the flasks from the boiling water and, to stop any further reaction, dilute with distilled water at once to slightly less than final volume. Cool the flasks to room temperature in tap water and make a final adjustment to volume. The developed color is stable for several hours.

Determine the absorption at 520 mμ of the developed color of each solution against distilled water in a photometer. The absorption of the picrate blank should be very low and constant (< 0.004) at this wave length.

Prepare a graph of absorption against equivalent hydrogen cyanide concentrations of 0.05, 0.10, 0.25, and 0.50 mg. per 100 ml. The absorption of the picrate blank need not be used in the graph. If the procedure has been followed carefully, the standard curve will be a straight line.

Calculation

Read the hydrogen cyanide concentration from the standard curve for the absorption obtained in the analysis. Calculate the amount of cyanides in the sample gas by the following equation:

$$\text{Cyanides, per cent by volume as HCN} = \frac{77.2E}{B\,D\,V}$$

where E = hydrogen cyanide, milligrams, read from standard curve

B = volume of aliquot taken from distillate, milliliters

D = volume of aliquot taken for distillation, milliliters

V = volume of gas sample, cubic feet, at 60°F. and 1 atm.

$$77.2 = \left[\frac{100\ \text{(ml. of dist.)}}{1000\ \text{(mg. per g.)}}\right]\left[\frac{23.6\ \text{(liters per mol)}}{27\ \text{(M.W. of HCN)}}\right]\left[\frac{\text{(ml. of absorber solution)}}{28.3\ \text{(liters/cu. ft.)}}\right]100(\%)$$

## 5 Analytical Procedure for Aldehydes*

Reaction

Sodium bisulfite adds to an aldehyde according to the following equation:

$$RCHO + NaHSO_3 = RCH(OH)SO_3Na$$

---

* Goldman, F. H., and Yagoda, H., "Collection and Estimation of Formaldehyde in the Air," Ind. and Eng. Chem. (Anal. Ed.) 15, 377 (1943)

## Reagents

1 per cent fresh sodium bisulfite solution, pH = 2.7
Starch indicator solution for iodimetric titration
Standard 0.1N iodine solution
Standard 0.05N sodium thiosulfate solution
Buffer solution: 80 g. of $Na_2CO_3$, 20 ml. of glacial acetic acid made up to a liter with distilled water, pH = 9.6

## Procedure

After the sample is taken in the 2 liter evacuated flask containing 10 ml. of the sodium bisulfite solution, it should be allowed to stand for at least 20 minutes. The contents are then transferred to a 250 ml. Erlenmeyer flask. Add 2 ml. of starch indicator solution and 0.1N iodine solution, just sufficient to obtain a dark blue color. Carefully wash down the sides of flask. Decolorize by adding a drop or two of 0.05N sodium thiosulfate solution and bring to faint blue color with 0.005N iodine.

Chill thoroughly in an ice bath, add 50 ml. of thoroughly chilled buffer solution and allow to stand in ice bath for 10 minutes. Titrate the liberated bisulfite with 0.005N iodine to the same faint blue color end point.

Run a blank using the same quantities of reagents and substract it from the titration.

## Calculations

The sample volume is corrected to 60°F. and 760 mm. Hg.

$$\text{PPM as HCHO} = \frac{(\text{ml. of } I_2)\,(N) \times 11.8 \times 10^3}{\text{corr. vol. in liters}}$$

N = normality of iodine solution

## Note

The efficiency of this method for the determination of aldehydes decreases as higher homologs are encountered. For a 2 liter sample, results are reported to the nearest 1 p.p.m.

## 6 Analytical Procedure for Oxides of Nitrogen* (Phenoldisulfonic Acid Method)

### Reagents

Absorbing Solution:

An absorbing solution is prepared by adding 1 ml. of 3 per cent hydrogen peroxide to 100 ml. of 0.1N sulfuric acid. Twenty-five ml. of this freshly prepared absorbing solution is added to each of the 2 liter sample flasks and about 50 ml. is retained for running solution blanks.

Phenoldisulfonic Acid Solution:

Dissolve 25 g. of pure phenol in 150 mL of concentrated sulfuric acid on a steam bath, cool and add 75 ml. of fuming sulfuric acid (15 per cent $SO_3$) Heat to 100°C. for 2 hours. Store in a brown, glass-stoppered bottle. This solution will be colorless if prepared from pure reagents. It will deteriorate on long standing and yield a high blank.

1 N (approx.) sodium hydroxide solution
conc. sulfuric acid
conc. ammonium hydroxide

### Procedure

The sample is allowed to stand at least 6 hours to insure complete absorption of the oxides of nitrogen. When absorption is complete, all oxides of nitrogen with the exception of nitrous oxide ($N_2O$) will be converted to nitric acid. The following reactions are involved in the case of nitrogen dioxide:

$$2NO + H_2O = HNO_2 + HNO_3$$

$$HNO_2 + H_2O_2 = HNO_3 + H_2O$$

The contents of the 2 liter sampling flask are transferred quantitatively to a 200 ml. casserole, and the solution is made alkaline to litmus with 1N sodium hydroxide solution.

* "Analytical Procedure for Oxides of Nitrogen, Phenoldisulfonic Acid Method," APCD Research Division Methods

A blank is prepared by placing 25 ml. of original absorbing solution in a casserole, diluting to approximately the same volume as the sample and making alkaline to litmus. The solutions are then evaporated to dryness on a steam bath.

Cautiously add 1 ml. of phenoldisulfonic acid solution to the dry residue and triturate thoroughly with a glass rod. Add 1 ml. of water and 4 drops of concentrated sulfuric acid. Heat on a steam bath for 3 minutes with occasional mixing. Cautiously add 25 ml. of water followed by 5 ml. of concentrated ammonium hydroxide. A yellow color is developed. Filter the solution and dilute to 50 ml.

The light absorption of the solution is measured in a Klett-Summerson photoelectric colorimeter using a blue (No. 42) light filter and a 20 mm. light path. The colorimeter may be zeroed against the blank, or against distilled water and the blank value subtracted from each reading. The weight of nitrogen dioxide in the sample is obtained from a standard colorimeter chart prepared from known standard potassium nitrate solutions.

## Calculations

$$\text{mg. of nitrogen dioxide per standard cubic foot} = \frac{W \times 28.3}{V_c \times 10^3}$$

$$\text{p.p.m. (vol.) of nitrogen dioxide} = \frac{W \times 23.7 \times 10^6}{46\ V_c}$$

where $W$ = weight of nitrogen dioxide in grams
$V_c$ = volume of sample in liters corrected to 760 mm. Hg and 60°F.

## Notes and Comments

1. The more concentrated samples may yield colors too dark to be read on the colorimeter. The sample may be diluted with water. An alternative is to use a smaller sampling flask.

2. Since hydrogen peroxide is necessary to change the nitrite to nitrate, an adequate amount is necessary. The amount should always be in excess over oxidizable material in the sample.

3. Inorganic nitrates or organic nitrogen compounds which are easily oxidized will interfere with this method, giving high results.

4. The sensitivity of this method has been found to be about 5 p.p.m.

## 7 Infrared Spectrophotometric Method for* Determination of Hydrocarbons

The contents of a two-liter flask are purged into the one-meter cell of a modified Beckman I.R. 2 dispersion type spectrophotometer. This is a standard model modified by the use of a one-meter cell, operated at approximately four times the intended gain and 1/7 the minimum intended scanning speed and at a maximum damping.

The sample is analyzed by scanning the spectrum over the three to four micron range and measuring the optical density, corrected for blank, at approximately 3.45 microns. Absorbance at this wavelength is attributed to the carbon-hydrogen stretching bond.

The instrument is calibrated against specially distilled n-hexane and all results are expressed in terms of n-hexane. The results of the analyses first relate to a given weight of hexane and this is subsequently converted into the equivalent volume relationship.

A sample is fed directly into the cell (no drying traps are used) by attaching the flask to the one-meter cell which has been evacuated. The pressure in the cell is recorded.

## 8 Analysis of Stack Gases by Mass Spectrometer**

### Scope

1. This method describes the mass spectrometric determination of $C_1$ through $C_6$ hydrocarbons, and other organic and inorganic compounds normally found in refinery stack gases.

### Outline of Method

2. Samples are analyzed by mass spectrometry using peaks at masses 2, 15, 18, 22, 26, 27, 30, 32, 34, 39, 42, 43, 44, 48, 54, 56, 57, 58, 60, 62, 64, 70, 72, 84, 86. Calculations are based on the calibration data

---

* For a more detailed description of the Infrared Spectrophotometer used, and method of calibration, see Mader, et. al., "Determination of Small Amounts of Hydrocarbons in the Atmosphere," Analytical Chemistry, Vol 24, pp. 1899 (Dec. 1952)

** This method is presented as submitted by Mr. Davis A Skinner, Air Pollution Adviser, Union Oil Co. of California, Research Department.

of those compounds expected in the mixture. Where possible , components are calculated on an individual basis. Where isomers exist and components cannot be calculated individually, analyses are made on the basis of compound types. These include $C_6$ paraffins, $C_6$ olefins + $C_6$ naphthenes (these types cannot be resolved), $C_6$ olefins + cyclopentane (these also cannot be resolved) and butenes. Results are expressed in mole per cent.

Definitions

3. (a) The parent peak of a compound is the peak whose mass corresponds to the molecular weight of the compound.

(b) The base peak of a compound is the peak used to calculate the concentration of that compound in a mixture. Usually it is the parent peak of the compound.

(c) A polyisotopic peak is one which is composed in part of contributions from ions which are normally of lesser mass but which contain heavy isotopes and hence appear as fragments of higher mass.

(d) A monoisotopic peak is one which arises from ions containing only one isotope of each of the atoms comprising the ion.

(e) Base peaks for each compound are as follows:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $H_2$ | 2 | $H_2S$ | 34 | $CH_3SH$ | 48 | $C_2H_5SH$ | 62 |
| $CH_4$ | 15 | $C_3H_4$ | 39 | $C_4H_6$ | 54 | $SO_2$ | 64 |
| $H_2O$ | 18 | $C_3H_6$ | 42 | $C_4H_8$ | 56 | $C_5H_{10}$* | 70 |
| $CO_2$ | 22 | $C_3H_8$ | 44 | $iC_4H_{10}$ | 58 | $iC_5H_{12}$ | 72 |
| $C_2H_2$ | 26 | | | $nC_4H_{10}$ | 58 | $nC_5H_{12}$ | 72 |
| $C_2H_4$ | 27 | | | COS | 60 | $C_6H_{12}$** | 84 |
| $C_2H_6$ | 30 | | | | | $C_6H_{14}$ | 86 |
| $O_2$ | 32 | | | | | | |

* Includes $C_5$ olefins and cyclopentane
** Includes $C_6$ olefins and $C_6$ naphthenes

(f) Sensitivity - Divisions of peak height per micron of pressure.

(g) Gross peak - Total peak height, including peak height caused by a specific component and contributions from any other component that may fragment in a manner to contribute.

(h) Net peak - Peak height with contributions from all other components removed, the remainder being caused by one specific component.

## Apparatus

4. Consolidated Electro Dynamic Corporation mass spectrometer Model 21-101, modified to Model 21-103, including high speed amplifier.

Mass spectrometer operating conditions:

1. Magent current .595 amperes.
2. Ionizing current 100 micro amperes (normal 10 micro amperes).
3. Amplifier at high sensitivity.

## Procedure

5. (a) Before the mass spectrometer ionizing current is increased to 100 micro amps, a normal butane pattern is run to establish the ratio of sample peak sensitivities to peak sensitivities obtained previously from calibration runs. (Reference - Consolidated Engineering Corporation Mass Spectrometer Computing Manual 1, 4:06).

(b) Pure $H_2$ or He, in equilibrium with pure water vapor is introduced into the mass spectrometer at about 100 microns pressure. This mixture is scanned from mass 2 to 86 to measure the instrument background. The mixture is then pumped out and the sample admitted, also at about 100 microns pressure, and scanned from mass 2 to 86.

## Calculations

6. Three basic calculation procedures are used to reduce the gross polyisotopic base peak to a net polyisotopic base peak. These procedures may be used alone or in conjunction with each other.

(a) Isotope correction, (Ref. - Consolidated Engineering Corporation, Mass Spectrometer Computing Manual II, Table B:01) where the interference on the base peak of a compound by other components is only through isotopes.

Set a = gross base peak height

b = gross peak height of peak immediately preceding a

c = isotope factor for b

d = monoisotopic base peak

e = net polyisotopic base peak

f = polyisotopic base peak contribution to b (pattern)*

*(Ref. Consolidated Engineering Corporation Computing Manual I, 1:07)

Then $a - cb = d$

and $dfc - d = e$

(b) Simultaneous equations (Ref. - Consolidated Mass Spectrometer Computing Manual II, A:01)

(c) Direct subtraction of contributions from heavier components where these are calculated in turn in order of decreasing molecular weight using base peaks and polyisotopic patterns, i.e., $a = b - \lesssim p_i k_i$ where

a = net base peak height

b = gross base peak height

$p_i$ = magnitude of base peak of component i

$k_i$ = pattern of component i contributing to b

Measure peak heights and subtract background peaks to give a gross peak heights caused by components in the stack gas.

The 22 peak ($CO_2$ base peak) is caused entirely by $CO_2$. The $CO_2$ contribution to the 44 peak is determined by using the $CO_2$ 22-44 pattern. Propane is calculated from the 44 peak by reducing the residual 44 peak to a polyisotopic propane peak as shown in 6 (a). Propane contributions to all lower masses are then calculated using the polyisotopic propane pattern.

All other components are determined in order of decreasing molecular weight starting with the heaviest components seen to be present. If $C_6$ paraffins are present, an average $C_6$ pattern is used, since normally these isomers cannot be resolved and calculated individually. Unless some outside information is available regarding the composition of the hexane isomers, a pattern based on equal parts of each isomer is used. Using this pattern in conjunction with the measured base peak, contributions of the hexanes to all lower masses can then be determined. Similarly, a $C_6$ olefin-naphthene pattern is calculated using equal parts of each compound. In this case, the olefins and naphthenes cannot be resolved, so that it is necessary to average all compounds of both types. Using the base peak which has been cleared of interference from the hexanes (as described in 6 (c) ) in conjunction with the average pattern, the interference of this group on lower masses is calculated.

$C_5$ naphthene-olefins are then determined as a total, since the two types cannot be resolved. A pattern based on equal parts of $C_5$ olefins and cyclopentane is used in this calculation, as in the case of the $C_6$ naphthenes-olefins pattern. The contribution from $C_5$ paraffins to the $C_5$ naphthene-olefins base peak is negligible. Hence, no correction is needed for this interference before the calculation is made. The interference of the $C_5$ naphthene-olefins on lower masses is then determined.

Butanes and pentanes are obtained simultaneously by the use of a 4 x 4 inverted matrix (Ref. - Consolidated Engineering Corporation Computing Manual II, A:01) using masses 43, 57, 58 and 72. The polyisotopic patterns at mass 43 and 57 are corrected to monoisotopic patterns for use in the 4 x 4 matrix only. Therefore, the 43 and 57 peaks are made monoisotopic to eliminate the isotope interference of propene and butenes on these peaks. These peaks have been previously corrected for the interference of $C_6$ paraffins and $C_6$ olefins-naphthenes. The 58 and 72 peaks are left as polyisotopic values. Following the calculation of these four components, corrections for the interference of these components on lower masses is carried out using the respective patterns and base peaks.

Butenes are calculated next. An average pattern is established for this group, as in the case of the hexanes and combined $C_6$ olefins-naphthenes. Again, using the base butene peak corrected for interference from heavier components in conjunction with the average butene pattern, the interference of this group is calculated for all lower masses.

All other hydrocarbons of lower molecular weight, propene through methane, are calculated on an individual basis, in order of decreasing molecular weight. In each case, the interference of heavier components on the base peak is calculated, and in turn the interference of each compound is determined on lower molecular weight components using corrected base peaks and respective patterns. In the case of $C_2H_4$, a small isotopic contribution exists from the acetylene base peak. However, this is very small and can be neglected.

All non-hydrocarbons are calculated on an individual basis. In each case, as in the hydrocarbons, interferences are removed from the base peaks and in turn using base peaks and patterns, interferences are removed from lower molecular weight materials. In the case of $H_2S$, the only interference on the base peak arises from the heavy $O_2$ isotope, and this is readily corrected by using the $O_2$ calibration pattern.

In many cases, no $C_5$ or $C_6$ compounds can be seen in the stack gas spectrum. The butane concentration is low enough that the iso and normal butanes cannot be resolved. In this case it is necessary to use a butane pattern based on equal parts of the two isomers.

The partial pressure of each component, and the corresponding mole per cent are obtained from the following equations:

1. Partial pressure = $\frac{\text{net base peak height}}{\text{sensitivity of base peak} \times 10}$
2. Mole per cent = $\frac{\text{partial pressure} \times 100^*}{\text{corrected total observed pressure}}$

Calculation Check Peak

The 41 peak is not the parent peak or base peak of any component. It is composed entirely of fragment contributions from C3 - $C_6$ hydrocarbons. When the net base peak heights have been determined (described previously in method), their contributions to mass 41 are calculated using the respective patterns for each $C_3$ - $C_6$ hydrocarbon. The sum of these contributions should equal the 41 peak $\pm$ 2%

* Total observed pressure is corrected using ratio determined in 5 (a).



Reproduced from best available copy.

## Addendum I.

### Correction of M/E 15 For the Contribution of Nitrogen 15

The correction of m/e 15 for the contribution of nitrogen 15 must be made as part of the procedure in calculating methane concentrations. The correction for m/e 15 for contributions from heavier components can be made using a combination of parent peaks and respective pattern values at m/e 15. Nitrogen, however, is present in such high concentrations (about 80 mole per cent) in stack gases that both m/e 28 and m/e 14 are off scale, under conditions of large sample pressure and high ionizing current, and the usual procedure cannot be followed. In this case it is necessary to run pure nitrogen at high sensitivity and calculate a sensitivity for m/e 15 directly. The nitrogen concentration of the sample must be determined by a supplementary method such as Orsat analysis.

The contribution of nitrogen 15 to sample m/e 15 is then found by the following equation: Contribution of nitrogen 15 to total m/e 15 = (Sample pressure) (per cent nitrogen) (sensitivity of nitrogen 15).

## Addendum II.

### Noble Gas Isotopes

The presence of the noble gases in the atmosphere is not usually of interest in the mass spectrum of air under normal operating conditions. Argon at m/e 40 has an appreciable sensitivity and is generally carried as part of the air pattern, However, under mass spectrometer conditions of high sensitivity, other rare gases appear in the spectrum. Although they do not interfere with the analysis of the usual hydrocarbons and non-hydrocarbons found in stack gases, their presence may lead to some confusion in the interpretation of spectral data.

Argon has an isotope of m/e 36. The magnitude of this is about 0.3 per cent of the isotope at m/e 40. At the same time doubly ionized argon of m/e 40 gives rise to a peak at m/e 20, the magnitude of this peak being about 13 per cent of m/e 40. Neon m/e 20 and neon m/e 22 also appear in the spectrum; m/e 22 having a value of about 10 per cent of m/e 20. The presence of neon m/e 22 introduces a slight error in the calculation of carbon dioxide from the record m/e 22, but this error is negligible where the carbon dioxide concentration is greater than about 7 per cent. The presence of krypton and xenon have not been demonstrated. However, krypton with m/e 84, poses a possible threat of confusion with the parent masses of $C_6$ olefins and naphthenes. The possibility of the presence of krypton

should be considered if an unusual m/e 84 appears on the record without accompanying pattern peaks corresponding to olefins or naphthenes.

## ACKNOWLEDGEMENT

The Los Angeles County Air Pollution Control District's Source Testing Unit carried out the stack sampling program.

The mass spectrometric analyses of the stack gas samples were performed at the Union Oil Company of California Research Center and the Richfield Oil Corporation Research Center.

The aid of Mr. Robert L. Ramlo, Mr. Davis A. Skinner and Dr. L. M. Richards of the Los Angeles County Air Pollution Control District, the Union Oil Company of California, and the Richfield Oil Corporation, respectively, is gratefully acknowledged.